Anomalous relaxation in quantum systems and the non-Markovian stochastic Liouville equation.

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The kinetics of relaxation in quantum systems induced by anomalously slowly fluctuating noise is studied in detail. In this study two processes are considered, as examples: (1) relaxation in two-level system (TLS) caused by external noise with slowly decaying correlation function $P(t) \sim (wt)^{-\alpha}$, where $0 < \alpha < 1$, and (2) anomalous-diffusion controlled radical pair (RP) recombination in which relaxation results from the reaction with slowly fluctuating reaction rate whose fluctuations are governed by subdiffusive relative motion of radicals in a potential well. Analysis of these two processes is made within continuous time random walk approach (CTRWA). Rigorous CTRWA-treatment of the processes under study results in the non-Markovian stochastic Liouville equation (SLE) for the density matrix of the systems. This SLE predicts important specific features of relaxation kinetics of quantum systems in the presence of the above mentioned anomalous noise. In TLS, for example, relaxation of both phase and population turns out to be anomalously slow and strongly non-exponential. Moreover, for $\alpha < 1$ in the limit of characteristic fluctuation rates w much larger than the frequency of quantum transitions ω_s ($w/\omega_s \gg 1$) the relaxation kinetics in TLS is independent of w. Strong changes of the relaxation kinetics is found with the change of w and α. In RP recombination the anomalous fluctuations of reaction rate (due to anomalous diffusion) show themselves in non-analytical dependence of the reaction yield Y_r on reactivity and parameters of the RP spin Hamiltonian. In particular, the spectrum shape of reaction yield detected magnetic resonance, i.e. the dependence of Y_r on the frequency ω of resonance microwave field is found to be strongly non-Lorenzian with the width to be determined by the strength ω_1 of this field.

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I. INTRODUCTION

The noise induced relaxation in quantum systems is very important process, which is investigated in various brunches of physics and chemistry: magnetic resonance [1], quantum optics, nonlinear spectroscopy [2], solid state physics [3, 4], etc.

Some of these processes are analyzed assuming fast decay of correlation functions of this noise τ_c and considering the short correlation time limit (SCTL). This approach is well known in the general relaxation theory [5]. In the absence of memory the relaxation is described by very popular Bloch-type equations. Nevertheless, in a large number of other processes the memory effects come to play. Important steps beyond the conventional short correlation time approximation can be made within the approach treating the relaxation kinetics with the stochastic Liouville equation (SLE) [6]. This approach, however, also has strong limitations: it assumes the noise fluctuations to be Markovian. The alternative approach, which can be applied for the analysis memory effects is based on the Zwanzig projection operator formalism [7]. Unfortunately, in reality the projection formalism allows for tractable analysis of the memory effects only in the lowest orders in the fluctuating interaction V inducing relaxation [8].

At present especially significant interest to the correct interpretation of long memory (non-Markovian) effects has been excited by recent works concerning processes governed by noises whose correlation functions $P(t)$ decay anomalously slowly: $P(t) \sim t^{-\alpha}$ with $\alpha < 1$. A large number of different phenomena, in which these processes play important role, are considered in the review article [9]. Some of them are discussed in relation to spectroscopic studies of quantum dots [10, 11]. Similar problems are analyzed in the theory of stochastic resonances [12]. Many works study the manifestation of non-Markovian long memory effects in dielectric relaxation and linear dielectric response [13] (and references therein). All anomalous relaxation processes mentioned above cannot be properly described by any methods based on the short correlation time approximation. The conventional SLE approach is not appropriate for description of these processes either.

The efficient method of analyzing the memory effects (including the case of anomalously long memory) has recently been developed in ref. [14]. It treats the noise within the continuous time random walk approach (CTRWA) [15, 16, 17], describing the statistical properties of the noise in terms of the probability distribution functions (PDFs) of renewals of the interaction fluctuations associated with the noise. The developed CTRWA-based method is based on the Markovian representation of the any CTRW-processes by the Markovian ones proposed in ref. [14]. This representation allows for obtaining the formal matrix expression for the evolution operator of the system under study, which can be considered as the non-Markovian generalization of the conventional SLE [14] and is called hereafter the non-Markovian SLE.

The non-Markovian SLE appeared to be very fruit-

ful for description of some classical processes assisted by stochastic anomalous spatial migration [18]. The memory effects are known to manifest themselves in this processes extremely strongly leading to strongly non-exponential anomalous relaxation kinetics [19, 20, 21].

In this work the proposed non-Markovian SLE is applied to the detailed analysis of specific features of relaxation in quantum systems induced by anomalous noise, i.e. the noise with anomalously long-tailed correlations in time, whose effect on quantum systems can hardly be correctly treated by expansion in powers of the noise amplitude. This type of the SLE enables one to describe relaxation kinetics without expansion in the fluctuating interaction. In some physically reasonable approaches, for example in the sudden relaxation model (SRM), it allows for describing the phase and population relaxation kinetics in analytical form. In the work two types of processes are considered: relaxation in two-level systems (TLS) and anomalous-diffusion assisted radical pair (RP) recombination in a potential well, as an example of processes in multilevel systems. Relaxation in these systems is shown to be strongly non-exponential. In addition, in RP recombination anomalous properties of relaxation (caused by anomalous relative diffusion) result in some peculiarities of magnetic field effects [22]: non-analytical dependence of magnetic field affected recombination yield (MARY) on the parameters of the spin Hamiltonian, strongly non-Lorenzian shape of lines of reaction yield detected magnetic resonance (RYDMR) [22], etc.

II. GENERAL FORMULATION

We consider noise induced relaxation in the quantum system whose evolution is governed by the hamiltonian

$$H(t) = H_s + V(t), \tag{2.1}$$

where H_s is the term independent of time and $V(t)$ is the fluctuating interaction, which models the noise. The evolution is described by the density matrix $\rho(t)$ satisfying the Liouville equation ($\hbar = 1$)

$$\dot{\rho} = -i\hat{H}(t)\rho, \;\text{ with }\; \hat{H}\rho = [H,\rho] = [H\rho - \rho H]. \tag{2.2}$$

$V(t)$-fluctuations are assumed to be symmetric ($\langle V\rangle = 0$) and result from stochastic jumps between the states $|x_\nu\rangle$ in the (discrete or continuum) space $\{x_\nu\} \equiv \{x\}$ with different $V = V_\nu$ and $H = H_\nu$ (i.e. different $\hat{V} = \hat{V}_\nu \equiv [V_\nu, \dots]$ and $\hat{H} = \hat{H}_\nu$):

$$\hat{\mathcal{V}} = \sum\nolimits_\nu |x_\nu\rangle\hat{V}_\nu\langle x_\nu| \;\text{ and }\; \hat{\mathcal{H}} = \sum\nolimits_\nu |x_\nu\rangle\hat{H}_\nu\langle x_\nu|. \tag{2.3}$$

Hereafter we will apply the bra-ket notation:

$$|k\rangle, \quad |kk'\rangle \equiv |k\rangle\langle k'|, \;\text{ and }\; |x\rangle \tag{2.4}$$

for the eigenstates of H (in the original space) and $\hat{H}$ (in the Liouville space), and for states in $\{x\}$-space, respectively.

It is worth noting that within the proposed semiclassical approach one can also describe some fluctuating irreversible processes in the system modelled by the additional non-Hermitian relaxation term $-i\hat{K}(t)$ in the Liouville operator $\hat{H}$. In this model the effect of fluctuating irreversible process results in modification of the Liouville equation (2.2):

$$\dot{\rho} = -i\hat{L}\rho, \;\text{ in which }\; \hat{L} = \hat{\mathcal{H}} - i\hat{\mathcal{K}}. \tag{2.5}$$

In the majority of processes the time evolution of observables under study is determined by the evolution operator $\hat{\mathcal{R}}(t)$ in the Liouville space averaged over $V(t)$- and $K(t)$-fluctuations:

$$\rho(t) = \hat{\mathcal{R}}(t)\rho_i, \;\text{ where }\; \hat{\mathcal{R}}(t) = \left\langle Te^{-i\int_0^t d\tau \hat{L}(\tau)}\right\rangle. \tag{2.6}$$

The operator $\hat{\mathcal{R}}(t)$ can equivalently be represented in terms of the conditional evolution operator $\hat{\mathcal{G}}(x, x'|t)$ averaged over the initial distribution $P_i(x)$:

$$\hat{\mathcal{R}}(t) = \langle\hat{\mathcal{G}}\rangle \equiv \sum\nolimits_{x,x_i} \hat{\mathcal{G}}(x, x_i|t)P_i(x_i). \tag{2.7}$$

For steady state $V(t)$-fluctuations the averaging should be made over the equilibrium distribution $P_e(x)$, i.e. $P_i(x) = P_e(x)$.

It is worth noting, however, that evaluation of some observables requires analysis of the conditional operator $\hat{\mathcal{G}}(x, x_i|t)$ itself rather than the averaged one $\hat{\mathcal{R}}(t)$ (see Sec. IVC).

Thus, in the proposed semiclassical approximation for $V(t)$- and $K(t)$-fluctuations the relaxation kinetics is determined by the operator $\hat{\mathcal{G}}(x, x_i|t)$. Its evaluation is, in general, a complicated problem. In what follows we will discuss important approaches in which this problem can be significantly simplified by reducing it to solving the (differential or integral) SLE for $\hat{\mathcal{G}}(x, x_i|t)$ [6].

In our further study we will often use the Laplace transformation of functions under study in time t conventionally denoted as

$$\widetilde{Z}(\epsilon) = \int_0^\infty dt\, Z(t)e^{-\epsilon t} \tag{2.8}$$

for any function $Z(t)$.

III. STOCHASTIC LIOUVILLE EQUATIONS

The goal of our work is to analyze the strong memory effects within the CTRWA. This approach is known to result in the complicated non-Markovian SLE [14] for $\hat{\mathcal{G}}(x, x_i|t)$. However, it is instructive to start the discussion with the simpler Markovian models reducing to the conventional semiclassical SLE.

A. Markovian fluctuations

In the Markovian approach the kinetics of jumps in $\{x\}$-space leading to $V(t)$-fluctuations are described by the PDF $P(x,t|x_i,t_i)$ satisfying equation [5]

$$\dot{P} = -\hat{\mathcal{L}}P \quad \text{with} \quad P(x,t_i|x_i,t_i) = \delta_{xx_i}, \tag{3.1}$$

where $\hat{\mathcal{L}}$ is some linear operator. The principal simplification of the problem results from the fact that in the Markovian approach (3.1) the $\hat{\mathcal{G}}(x,t|x_i,t_i)$ obeys the SLE [6]:

$$\dot{\hat{\mathcal{G}}} = -(\hat{\mathcal{L}} + i\hat{L})\hat{\mathcal{G}}, \text{ where } \hat{\mathcal{G}}(x,t_i|x_i,t_i) = \delta_{xx_i}, \tag{3.2}$$

so that in accordance with eq. (2.7) we get for the Laplace transform $\tilde{\hat{\mathcal{R}}}$:

$$\tilde{\hat{\mathcal{R}}} = \langle \tilde{\hat{\mathcal{G}}} \rangle = \langle (\epsilon + i\hat{L} + \hat{\mathcal{L}})^{-1} \rangle \tag{3.3}$$

The idea of the SLE (3.2) is based on the simple observation that the changes of $\hat{\mathcal{G}}$ resulted from dynamical motion [eq. (2.2)] and stochastic evolution [eq. (3.1)] during short time Δt are written as

$$\Delta_d\hat{\mathcal{G}} = -(i\hat{L}\hat{\mathcal{G}})\Delta t \text{ and } \Delta_f\hat{\mathcal{G}} = -(\hat{\mathcal{L}})\hat{\mathcal{G}})\Delta t, \tag{3.4}$$

respectively, so that total change of $\hat{\mathcal{G}}$ is given by the expression

$$\Delta\hat{\mathcal{G}} = \Delta_f\hat{\mathcal{G}} + \Delta_d\hat{\mathcal{G}} = -(\hat{\mathcal{L}} + i\hat{L}))\hat{\mathcal{G}}\Delta t, \tag{3.5}$$

equivalent to eq. (3.2).

B. Non-Markovian fluctuations

1. Continuous time random walk approach

Non-Markovian $V(t)$-fluctuations can conveniently be described by the CTRWA [which leads to the non-Markovian SLE [14] for $\hat{\mathcal{G}}(t)$]. It treats fluctuations as a sequence of sudden changes of $\hat{V}$. The onset of any particular change of number j is described by the matrix $\hat{P}_{j-1}$ (in $\{x\}$-space) of probabilities not to have any change during time t and its derivative $\hat{W}_{j-1}(t) = -d\hat{P}_{j-1}(t)/dt$, i.e. the PDF-matrix for times of waiting for the change. These matrices are diagonal and independent of j at $j > 1$:

$$\hat{P}_{j-1}(t) = \hat{P}(t),\ \hat{W}_{j-1}(t) = \hat{W}(t) = -d\hat{P}(t)/dt. \tag{3.6}$$

For $j = 1$

$$\hat{P}_0(t) \equiv \hat{P}_i(t) \text{ and } \hat{W}_0(t) \equiv \hat{W}_i(t) = -d\hat{P}_i(t)/dt \tag{3.7}$$

depend on the problem considered. For non-stationary (n) and stationary (s) fluctuations [15, 16, 17]

$$\hat{W}_i(t) = \hat{W}_n(t) = \hat{W}(t), \tag{3.8}$$

$$\hat{W}_i(t) = \hat{W}_s(t) = \hat{\tau}_e^{-1}\int_t^\infty d\tau\, \hat{W}(\tau), \tag{3.9}$$

respectively, where $\hat{\tau}_e = \int_0^\infty dt\, t\hat{W}(t)$ is the matrix of average times of waiting for the change [15, 16, 17].

It is worth noting some relations for the Laplace transforms of $\hat{W}_j(t)$ and $\hat{P}_j(t)$ suitable for our further analysis: $\tilde{\hat{P}}_j(\epsilon) = [1 - \tilde{\hat{W}}_j(\epsilon)]/\epsilon$ and $\tilde{\hat{W}}_s(\epsilon) = \tilde{\hat{P}}(\epsilon)/\hat{\tau}$ [15, 16, 17], as well as the representations

$$\tilde{\hat{W}}(\epsilon) = [1 + \hat{\Phi}(\epsilon)]^{-1} \text{ and } \tilde{\hat{P}}(\epsilon) = [\epsilon + \epsilon/\hat{\Phi}(\epsilon)]^{-1}. \tag{3.10}$$

in terms of the auxiliary matrix $\hat{\Phi}(\epsilon)$ diagonal in $\{x\}$-space (see below).

2. Markovian representation of CTRWA

In this Section we will briefly discuss the Markovian representation of the CTRWA recently proposed in ref. [14], which appears to be very useful for the CTRWA-based analysis of the problem under study and, in particular, provides the most rigorous method of deriving the non-Markovian SLE.

Suppose that the kinetics of $(\nu \to \nu')$-transitions in $\{x\}$-space is controlled by the Markovian process in another $\{q_j\}$-space, which is governed by the operator $\hat{\Lambda}$. The corresponding PDF $\sigma(j,t)$ satisfies equation

$$\dot{\sigma} = -\hat{\Lambda}\sigma \tag{3.11}$$

describing evolution in $\{q_j\}$-space and equilibration if the operator $\hat{\Lambda}$ has the equilibrium state $|e_q\rangle$ ($\hat{\Lambda}|e_q\rangle = 0$). This state is represented as

$$|e_q\rangle = \sum\nolimits_j p_{q_j}^e|j\rangle,\ \langle e_q| = \sum\nolimits_j \langle j|,\ (\langle e_q|e_g\rangle = 1). \tag{3.12}$$

where p_j^e are the probabilities of equilibrium population of states in $\{q_j\}$-space.

The q_j-process is assumed to control the evolution in $\{x\}$-space as follows: $(\nu \to \nu')$-transitions occur with the rate $\kappa_{\nu'\nu}$ whenever the system visits the transition state $|t\rangle$ in $\{q_j\}$-space. Transitions can lead to the change in $|j\rangle$-state, i.e to $(|t\rangle \to |n\rangle)-$transition with $|n\rangle \neq |t\rangle$. For simplicity, we assume that $|n\rangle = |t\rangle$ as well as that $\hat{\Lambda}$ and $|t\rangle$-state are independent of the state in $\{x\}$-space.

The evolution of the system in $\{x \otimes q_j\}-$space is described by the PDF matrix $|\hat{\rho}\rangle$ obeying the SLE

$$|\dot{\hat{\rho}}\rangle = -(\hat{\Lambda} + i\hat{L} + \hat{K}_d - \hat{K}_o)|\hat{\rho}\rangle, \tag{3.13}$$

where

$$\hat{K}_d = \hat{\kappa}_d \otimes |t\rangle\langle t| \text{ and } \hat{K}_o = \hat{\kappa}_o \otimes |n\rangle\langle t| \tag{3.14}$$

are the transition matrices (operating in $\{x \otimes q_j\}$-space) are diagonal and non-diagonal in $\{x\}$-subspace, respectively, in which

$$\hat{\kappa}_d = \sum\nolimits_\nu |\nu\rangle\kappa_{\nu\nu}\langle\nu|,\ \ \hat{\kappa}_o = \sum\nolimits_{\nu,\nu'\neq\nu} |\nu\rangle\kappa_{\nu\nu'}\langle\nu'|. \tag{3.15}$$

and $\kappa_{\nu\nu} = \sum_{\nu'(\neq\nu)} \kappa_{\nu'\nu}$. Equation (3.13) should be solved with the initial condition

$$|\hat{\rho}\rangle_{t=0} = |i\rangle \sum\nolimits_{\nu} |\nu\rangle\langle\nu|, \qquad (3.16)$$

where $|i\rangle = \sum_j p^i_{q_j} |j\rangle$, with $\langle e_q|i\rangle = \sum_j p^i_{q_j} = 1$.

The function of interest is the (time) Laplace transformed PDF in $\{x\}$-space

$$\tilde{\hat{\mathcal{G}}} = \langle e_q|\tilde{\hat{\rho}}\rangle = \sum\nolimits_j \tilde{\hat{\rho}}_j, \text{ in which } \tilde{\hat{\rho}}_j = \langle j|\tilde{\hat{\rho}}\rangle. \qquad (3.17)$$

It is determined by solution $|\tilde{\hat{\rho}}(\epsilon)\rangle$ of equation

$$|\tilde{\hat{\rho}}\rangle = \hat{G}|i\rangle + \hat{G}\hat{K}_o|\tilde{\hat{\rho}}\rangle, \qquad (3.18)$$

where

$$\hat{G} = (\hat{\Omega} + \hat{\Lambda} + \hat{K}_d)^{-1} \text{ with } \hat{\Omega} = \epsilon + i\hat{L}. \qquad (3.19)$$

The expression for $\tilde{\hat{\mathcal{G}}}$, obtained by solving eq. (3.18), can be represented in a CTRWA-like form, which in what follows [by analogy with the Markovian model (3.1)-(3.3)] will be treated as the solution of the so called non-Markovian SLE [14].

Hereafter, for brevity, we will sometimes omit the argument $\hat{\Omega}$ of the Laplace transforms of functions under study if this does not result in confusions.

3. Non-Markovian SLE

Solution of eq. (3.18) leads to the following non-Markovian SLE, written in matrix resolvent form [14],

$$\tilde{\hat{\mathcal{G}}} = \tilde{\hat{P}}_i(\hat{\Omega}) + \tilde{\hat{P}}_n(\hat{\Omega})[1 - \hat{\mathcal{P}}\widetilde{\hat{W}}_n(\hat{\Omega})]^{-1}\hat{\mathcal{P}}\widetilde{\hat{W}}_i(\hat{\Omega}), \qquad (3.20)$$

where

$$\hat{\mathcal{P}} = \hat{\kappa}_o/\hat{\kappa}_d \text{ with } \sum\nolimits_{\nu} \mathcal{P}_{\nu\nu'} = 1 \qquad (3.21)$$

is the matrix of jump probabilities with zeroth diagonal elements and $\widetilde{\hat{W}}_\mu$ ($\mu = n, i$) are written as

$$\widetilde{\hat{W}}_\mu = \hat{\kappa}_d\hat{G}_\mu, \text{ with } \hat{G}_\mu = (1 + \hat{g}_t\hat{\kappa}_d)^{-1}\hat{g}_\mu \qquad (3.22)$$

in which

$$\hat{g}_\mu = \langle t|(\hat{\Omega} + \hat{\Lambda})^{-1}|\mu\rangle, \quad \hat{g}_t = \langle t|(\hat{\Omega} + \hat{\Lambda})^{-1}|t\rangle. \qquad (3.23)$$

The non-Markovian SLE (3.20) can also be represented in an alternative convenient form [14]

$$\begin{aligned} \tilde{\hat{\mathcal{G}}} &= \tilde{\hat{P}}_i + \hat{\Omega}^{-1}\hat{\Phi}(\hat{\Phi} + \hat{\mathcal{L}})^{-1}\hat{\mathcal{P}}\widetilde{\hat{W}}_i & (3.24) \\ &= \tilde{\hat{P}}_{m_i} + \hat{\Omega}^{-1}\hat{\Phi}(\hat{\Phi} + \hat{\mathcal{L}})^{-1}\widetilde{\hat{W}}_{m_i}, & (3.25) \end{aligned}$$

where

$$\hat{\mathcal{L}} = 1 - \hat{\mathcal{P}} = 1 - \hat{\kappa}_o/\hat{\kappa}_d \qquad (3.26)$$

is the Kolmogorov-Feller-type operator describing the jump-like motion in $\{x\}$-space,

$$\hat{\Phi} = (\hat{g}_t - \hat{g}_n)\hat{g}_n^{-1} + (\hat{\kappa}_d\hat{g}_n)^{-1} \qquad (3.27)$$

is the matrix function (diagonal in $\{x\}$-space) characterizing $\hat{W}(t)$ [see eq. (3.10)]: $\widetilde{\hat{W}} = \widetilde{\hat{W}}_n = (1 + \hat{\Phi})^{-1}$, and

$$\widetilde{\hat{W}}_{m_i} = \widetilde{\hat{W}}_i/\widetilde{\hat{W}} \text{ and } \tilde{\hat{P}}_{m_i} = (1 - \widetilde{\hat{W}}_{m_i})/\hat{\Omega} \qquad (3.28)$$

are auxiliary (modified) PDF matrices of the type of waiting time PDFs.

The representation (3.25) of the non-Markovian SLE is somewhat different from that proposed in ref. [14]. Both representation are, however, equivalent and can equally be used for the analysis, though eq. (3.25) is closer in its form to the CTRWA-like expressions [3].

The operator $\hat{\mathcal{L}}$ is assumed to have the equilibrium eigenstate $|e_x^0\rangle$ (i.e. $\hat{\mathcal{L}}|e_x^0\rangle = 0$):

$$|e_x^0\rangle = \sum\nolimits_x P_e^0(x)|x\rangle \text{ and } \langle e_x^0| = \sum\nolimits_x \langle x|. \qquad (3.29)$$

The eigenstate $|e_x^0\rangle$, however, is not the true equilibrium state of the system under study. The true equilibrium state $|e_x\rangle$ is also determined by the behavior of $\hat{\Phi}(\epsilon)$ at $\epsilon \to 0$. It is clear from eq. (3.27) and definition of the PDF matrix $\hat{W}(t)$ that $\hat{\Phi}(0) = 0$, therefore, in general, we can write

$$\hat{\Phi}(\epsilon) \overset{\epsilon \to 0}{\sim} (\epsilon/\hat{w})^{\hat{\alpha}}, \text{ where } \hat{w} = \sum\nolimits_x |x\rangle w_x \langle x|. \qquad (3.30)$$

In this equation the matrices $\hat{\alpha}$ (of exponents) and $\hat{w}$ [of characteristic rates (see Sec. V)] are assumed to be diagonal in $\{x\}$-space. Moreover, for simplicity, to avoid analysis of exotic equilibrium states [14] we assume that $\hat{\alpha} \equiv \alpha$ is just a parameter independent of x rather than matrix. In accordance with formulas (3.25)-(3.27), for such α $\tilde{\hat{\mathcal{G}}} \overset{\epsilon \to 0}{\sim} (\epsilon + \hat{\mathcal{L}}\hat{w}^\alpha\epsilon^{1-\alpha})^{-1}$, i.e. the state $|e_x\rangle$ is, actually, the equilibrium eigenstate of $\hat{\mathcal{L}}\hat{w}^\alpha$ ($\hat{\mathcal{L}}\hat{w}^\alpha|e_x\rangle = 0$), which is written as

$$|e_x\rangle = N_w^{-1}\hat{w}^{-\alpha}|e_x^0\rangle \text{ with } N_w = \langle e_x^0|\hat{w}^{-\alpha}|e_x^0\rangle. \qquad (3.31)$$

Possible expressions for $|e_x\rangle$ in some particular models of $\hat{\mathcal{L}}$ are discussed below in Sec. IVA.

It is important to note that with the eigenstate $|e_x\rangle$ the average of any operator $\hat{Y}$ can be represented as

$$\langle\hat{Y}\rangle = \langle e_x|\hat{Y}|e_x\rangle. \qquad (3.32)$$

In particular, as it follows from eq. (2.6),

$$\hat{\mathcal{R}}(t) = \langle e_x|\hat{\mathcal{G}}|e_x\rangle \equiv \langle\hat{\mathcal{G}}\rangle. \qquad (3.33)$$

According to eqs. (3.20)-(3.22) the initial state $|i\rangle$ (in $\{q_j\}$) manifests itself only in the expressions for matrices $\hat{W}_i(t)$ and $\hat{P}_i(t)$. In particular [15, 16, 17]:

a) In the non-stationary n-CTRWA $|i\rangle = |n\rangle$, so that $\hat{\widetilde{W}}_i = \hat{\widetilde{W}}_n$, $\hat{\widetilde{P}}_i = \hat{\widetilde{P}}_n$ and

$$\hat{\widetilde{\mathcal{G}}}(\hat{\Omega}) = \hat{\widetilde{\mathcal{G}}}_n(\hat{\Omega}) = \hat{\Omega}^{-1}\hat{\Phi}(\hat{\Omega})[\hat{\Phi}(\hat{\Omega}) + \hat{\mathcal{L}}]^{-1}. \qquad (3.34)$$

b) In the stationary s-CTRWA $|i\rangle = |e\rangle$, where $|e\rangle$ is the equilibrium eigenstate [see eq. (3.12)], consequently $\hat{\widetilde{W}}_i = \hat{\widetilde{W}}_s = \hat{\widetilde{P}}_n/\hat{\tau}$, where $\hat{\tau} = \hat{g}_n\hat{\Phi}/p_t^e$ is the matrix of average times (diagonal in $\{x\}$-space) with $p_t^e = \langle t|e\rangle$. In the considered case $|n\rangle = |t\rangle$, when $\hat{\Phi} = 1/(\hat{\kappa}_d\hat{g}_t)$ and $\hat{\tau} = 1/(\hat{\kappa}_d p_t^e)$. Substitution of $\hat{\widetilde{W}}_s$ into eq. (3.20) yields

$$\hat{\widetilde{\mathcal{G}}}(\hat{\Omega}) = \hat{\widetilde{\mathcal{G}}}_s(\hat{\Omega}) = \hat{\Omega}^{-1} - \hat{\widetilde{\mathcal{G}}}_n(\hat{\Omega})\hat{\mathcal{L}}(\hat{\Omega}\hat{\tau})^{-1}, \qquad (3.35)$$

IV. USEFUL MODELS AND APPROACHES

A. Models for jump motion

1. *Sudden relaxation model (SRM).*

The SRM [14] assumes sudden equilibration in $\{x\}$-space described by operator

$$\hat{\mathcal{L}} = (1 - |e_0\rangle\langle e_0|)\hat{Q}^{-1}, \;\; \hat{Q} = 1 - \textstyle\sum_x P_x|x\rangle\langle x|, \qquad (4.1)$$

in which

$$|e_0\rangle = \textstyle\sum_x P_x|x\rangle, \;\; \text{and} \;\; \langle e_0| = \textstyle\sum_x\langle x|. \qquad (4.2)$$

is some auxiliary vector determined by the equilibrium vector $|e_x\rangle$:

$$|e_x\rangle = \textstyle\sum_x P_e(x)|x\rangle = \hat{q}|e_0\rangle \;\; \text{and} \;\; \langle e_x| = \langle e_0|, \qquad (4.3)$$

where

$$\hat{q} = N_0^{-1}\hat{Q}\hat{w}^{-\alpha} \;\; \text{with} \;\; N_0 = \textstyle\sum_x[(P_x - P_x^2)/w_x^\alpha]. \quad (4.4)$$

According to eqs. (4.3) and (4.4) :

$$P_x \; = \; \tfrac{1}{2} - \sqrt{\tfrac{1}{4} - N_0 w_x^\alpha P_e(x)}. \qquad (4.5)$$

This relation determines the vector $|e_0\rangle$ (in the definition of $\hat{\mathcal{L}}$) which ensures the given equilibrium state $|e_x\rangle$. The value of the parameter N_0 is fixed by the normalization condition for the distribution P_x:

$$\textstyle\sum_x \left[\tfrac{1}{2} - \sqrt{\tfrac{1}{4} - N_0 w_x^\alpha P_e(x)}\right] = 1. \qquad (4.6)$$

In the model (4.1) one gets for any $\hat{\widetilde{W}}_i$

$$\hat{\widetilde{\mathcal{R}}}_i = \langle\hat{\widetilde{P}}_{Q_i}\rangle + \langle\hat{q}^{-1}\widetilde{P}_Q\rangle[1 - \langle\hat{q}^{-1}\hat{\widetilde{W}}_Q\rangle]^{-1}\langle\hat{\widetilde{W}}_{Q_i}\rangle, \quad (4.7)$$

where $\hat{\widetilde{P}}_{Q_i} = (1 - \hat{\widetilde{W}}_{Q_i})/\hat{\Omega}$,

$$\hat{\widetilde{W}}_Q = (1 + \hat{\Phi}\hat{Q})^{-1}, \;\; \hat{\widetilde{W}}_{Q_i} = \hat{\widetilde{W}}_i(\hat{\widetilde{W}}_Q/\hat{\widetilde{W}}). \qquad (4.8)$$

The obtained general formulas are simplified in some particular models, for example, in the N-state SRM with

$$|e_0\rangle = N^{-1}\textstyle\sum_x|x\rangle, \; \hat{Q} = Q_N = 1 - N^{-1}, \qquad (4.9)$$

In this model $\hat{q} = \hat{w}^{-\alpha}/\sum_x w_x^{-\alpha}$. It is important to note that in the case of two states the model (4.9) is the only possible one.

Particularly simple expressions are obtained in the model of the only characteristic fluctuation rate:

$$\hat{w} \equiv w, \;\; \text{for which} \;\; |e_0\rangle = |e_x\rangle = N^{-1}\textstyle\sum_x|x\rangle. \quad (4.10)$$

For s-fluctuations this model assumes the average time $\hat{\tau}_e$ to be independent of x: $\hat{\tau}_e \equiv \tau_e$. Together with the model (4.9) it implies equipopulated equilibration with $\hat{q} = 1$ so that

$$\hat{\mathcal{L}} = Q_N^{-1}(1 - |e_x\rangle\langle e_x|) \;\text{and}\; \hat{\widetilde{W}}_Q = (1 + Q_N\hat{\Phi})^{-1}. \quad (4.11)$$

It predicts, for example, for n-fluctuations ($W_i = W$)

$$\hat{\widetilde{\mathcal{R}}} = \hat{\widetilde{\mathcal{R}}}_n = \langle\hat{\widetilde{P}}_Q\rangle[1 - \langle\hat{\widetilde{W}}_Q\rangle]^{-1}. \qquad (4.12)$$

The model (4.10) clearly reveals all important specific features of the non-Markovian-noise-induced relaxation in the simplest form.

2. *Diffusion model*

Another simple model allowing for analytical consideration of problem is the diffusion model. In this work the diffusion model will be applied to the analysis of recombination of the pair of radicals assuming that one of radicals undergoes isotropic diffusion in three dimensional space, say $\{\mathbf{r}\}$-space, while another radical does not move and is located at $\mathbf{r} = 0$. Conventionally, the diffusive motion of the moving radical is described by the Smoluchowski-type jump operator $\hat{\mathcal{L}} = 1 - \hat{\mathcal{P}}$ [14]. For simplicity we will consider isotropic processes for which

$$\hat{\mathcal{L}} = \hat{\mathcal{L}}_D = -\lambda^2 r^{-2}\nabla_r[r^2(\nabla_r + \nabla_r u_r)], \qquad (4.13)$$

where $r = |\mathbf{r}|$, $\nabla_r = \partial/\partial r$ is the gradient operator, λ^2 is the average square of the jump length independent of r, and $u_{\mathbf{r}}$ is the external interaction potential.

The potential u_r is assumed to be of the shape of (deep) spherically symmetric square well with the radius R much larger than the distance d of closest approach: $u_r = -u_0\theta(R - r)$ with $u_0 \gg 1$.

It worth noting that within the continuum model of stochastic jumps resulting in $V(t)$- and $K(t)$-fluctuations the corresponding operators $\hat{\mathcal{V}}$ and $\hat{\mathcal{K}}_r$ are just functions of $\mathbf{r}$. In the considered spherically symmetric case

$$\hat{\mathcal{V}} = \textstyle\sum_r |r\rangle\hat{V}_r\langle r| \;\; \text{and} \;\; \hat{\mathcal{K}} = \textstyle\sum_r |r\rangle\hat{K}_r\langle r|. \qquad (4.14)$$

B. Short correlation time limit (SCTL)

In practical applications of special importance is the SCTL for $V(t)$-fluctuations in which eq. (4.7) can markedly be simplified. It corresponds to the large characteristic (correlation) rate w_c of fluctuations, i.e. the large characteristic time of the dependence $\hat{\Phi}(\hat{\Omega})$: $w_c \gg \|V\|$. In our analysis we will discuss the general class of models for which $\hat{\Phi}(\hat{\Omega})$ is represented in the form $\hat{\Phi}(\hat{\Omega}) \equiv \hat{\Phi}(\hat{\Omega}/\hat{w})$. For such models the correlation rate can naturally be defined as $w_c = \|\hat{w}\|$.

In the SCTL the relaxation kinetics is described by the first terms of the expansion of $\hat{\Phi}(\hat{\Omega}/\hat{w})$ in small $\hat{\Omega}/w_c$, since $\hat{\Phi}(\epsilon)$ is the increasing function of ϵ with $\hat{\Phi}(\epsilon) \xrightarrow{\epsilon \to 0} 0$ [see Sec. IIB and, in particular, eq. (3.30)]. This fact allows one to significantly simplify the problem under study. Nevertheless, some important general conclusions can be made independently of the form of $\hat{\Phi}(\Omega)$ as it will be shown in Sec. V.

C. Models for quantum evolution.

Here we describe two systems which will be analyzed to illustrate the obtained general results: (1) the isolated quantum two-level system (TLS), whose relaxation results from $V(t)$-fluctuations described within the stochastic two-state model, and 2) the geminate pair of radicals diffusing in the potential well in which spin evolution, affected by the fluctuating reactivity $K(t)$, in turn strongly influences the reactivity.

1. Isolated quantum TLS

a. Two-level model. Quantum evolution of the TLS is governed by the hamiltonian (assumed to be real matrix) with

$$H_s = \tfrac{1}{2}\omega_s \sigma_z \;\text{ and }\; V = V_z\sigma_z + V_x\sigma_x, \qquad (4.15)$$

where

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \;\text{ and }\; \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \;\; \begin{array}{l} |+\rangle \\ |-\rangle \end{array}. \qquad (4.16)$$

b. Two-state model of fluctuations. In the two-state model of fluctuations $V(t)$-modulation is assumed to result from jumps between two states (in $\{x\}$-space), say, $|x_+\rangle$ and $|x_-\rangle$. It is important to note that in the particular case of two states any CTRWA-based kinetics model reduces to the simple two-state SRM [see eqs. (4.9) and (4.10)] in which $\hat{w} \equiv w$, $Q_2 = 1/2$, and

$$\hat{\mathcal{L}} = 2(1 - |e_x\rangle\langle e_x|) \;\text{ with }\; |e_x\rangle = \tfrac{1}{2}(|x_+\rangle + |x_-\rangle). \qquad (4.17)$$

c. Simple variants of TLS and two-state model. Below we will consider two examples of these models:

1) Diagonal noise [23]: $\omega_s = 0$, $\mathcal{V}_x = 0$, and $\mathcal{V}_z = \omega_0(|x_+\rangle\langle x_+| - |x_-\rangle\langle x_-|)$, therefore

$$H_{\nu=\pm} = \pm\tfrac{1}{2}\omega_0(|+\rangle\langle +| - |-\rangle\langle -|); \qquad (4.18)$$

2) Non-diagonal noise: $\mathcal{V}_z = 0$ and $\mathcal{V}_x = v(|x_+\rangle\langle x_+| - |x_-\rangle\langle x_-|)$, so that

$$H_{\nu=\pm} = H_s \pm v(|+\rangle\langle -| + |-\rangle\langle +|). \qquad (4.19)$$

In our further analysis the first model is applied to the description of dephasing while the second one is used in studying population relaxation.

d. Calculated observables. In the model (4.16) dephasing and population relaxation can be characterized by two functions:

1) The spectrum $I(\omega)$ which is taken in the form corresponding to Fourier transformed free-induction-decay (FTFID) experiments [24]

$$I(\omega) = \tfrac{1}{\pi}\mathrm{Re}\langle s|\hat{\tilde{\mathcal{R}}}(i\omega)|s\rangle; \qquad (4.20)$$

2) The difference of level populations

$$N(t) = \langle n|\hat{\mathcal{R}}(t)|n\rangle. \qquad (4.21)$$

In these two functions

$$|s\rangle = \tfrac{1}{\sqrt{2}}\big||+-\rangle + |-+\rangle\big\rangle \text{ and } |n\rangle = \tfrac{1}{\sqrt{2}}\big||++\rangle - |--\rangle\big\rangle. \qquad (4.22)$$

2. Model for reactive radical pairs

a. Magnetic field effects. The kinetics of RP recombination is known to be markedly affected by the RP spin evolution which is controlled by the spin Hamiltonian H of the pair. The dependence of the recombination kinetics on RP spin state results in a large number of phenomena called magnetic field effects [22].

In this work we will restrict ourselves to some simple and representative effects observed in strong magnetic field $\mathbf{B}$ for which the Zeeman interaction is much larger than the intraradical magnetic interactions (hyperfine interaction, etc.). We will also consider the effect of the external microwave field B_1 rotating with the frequency ω in the plane perpendicular to the vector $\mathbf{B}$.

For strong magnetic fields and in the presence of the field B_1 the spin Hamiltonian governing spin evolution of electrons in the pair of radicals, say a and b, can conveniently be written in the frame of reference rotating together with B_1 with the frequency ω [22]:

$$H_z = H_a + H_b \text{ with } H_\mu = (\omega_\mu - \omega)S_{\mu_z} + \omega_1 S_{\mu_x}, \qquad (4.23)$$

where $\mu = a, b$ and $\omega_\mu = g_\mu \beta B + \sum_j A_j^\mu I_{jz}$ is the Zeeman frequency of the radical μ possessing some paramagnetic nuclei with hyperfine interactions A_j^μ and $\omega_1 \approx \frac{1}{2}(g_a +$

$g_b)\beta B_1$. In case of need the matrix representation of the Hamiltonian (4.23) can be determined either in the bases of radical spin states $|\pm\rangle_a|\pm\rangle_b$ or in the basis of eigenstates of the total electron spin $\mathbf{S} = \mathbf{S}_a + \mathbf{S}_b$: singlet ($|S\rangle$) and triplet ($|T_{0,\pm}\rangle$) states, which are expressed as $|S\rangle = \frac{1}{\sqrt{2}}(|+\rangle_a|-\rangle_b - |-\rangle_a|+\rangle_b)$, $|T_0\rangle = \frac{1}{\sqrt{2}}(|+\rangle_a|-\rangle_b + |-\rangle_a|+\rangle_b)$, and $|T_\pm\rangle = |\pm\rangle_a|\pm\rangle_b$;

The RP recombination can be treated as a contact reaction at a distance of closest approach d using the simple model [22]

$$\hat{K}_r = k_0\hat{\kappa}_S\theta(r-d)\theta(d+\Delta-r), \qquad (4.24)$$

where

$$\hat{\kappa}_S = \{\mathcal{P}_s, \dots\} \qquad (4.25)$$

is anticommutator ($\{\mathcal{P}_s, \rho\} = \mathcal{P}_s\rho + \rho\mathcal{P}_s$) in which $\mathcal{P}_s = |S\rangle\langle S|$ is the operator of projection on the singlet ($|S\rangle$) spin state of RP.

The RP is assumed to be initially created in the singlet state $|S\rangle$ within the potential well at a distance $r = r_i < R$ ($r_i > d$), so that

$$\rho(r, t=0) \equiv \rho_i(r) = (4\pi r_i^2)^{-1}\delta(r - r_i)\mathcal{P}_s. \qquad (4.26)$$

b. Observables. In experiments on magnetic field effects a number of observables are discussed [22]. Here we analyze the most simple ones:

1) magnetically affected reaction yield (MARY) [22], measured in the external constant magnetic field,

2) reaction yield detected magnetic resonance (RYDMR) [22], i.e. microwave field influenced recombination yield.

In both types of experiments the observables under study are recombination (Y_r) and dissociation (Y_d) yields:

$$Y_r = (d/r_i)^2\Delta k_0 \mathrm{Tr}[\mathcal{P}_s\tilde{\hat{\mathcal{G}}}(d, r_i|\epsilon = 0)\mathcal{P}_s] \qquad (4.27)$$

and $Y_d = 1 - Y_r$.

Naturally, the expression (4.27) should be averaged over nuclear configurations (over ω_μ). However, in our further discussion we will omit this evident procedure and analyze the behavior of Y_r for fixed ω_a and ω_b (note that the case of fixed ω_a and ω_b can be realized experimentally, for example, with RPs which do not contain paramagnetic nuclei).

V. RESULTS AND DISCUSSION

A. Isolated quantum TLS

1. Some general results in the SCTL

a. Small $\|H_s\|/w_c \ll 1$. Within the SCTL relatively simple and general results can be obtained in the case $\|H_s\|/w_c \ll 1$. In the lowest order in $\|\hat{\Phi}(\hat{\Omega}/w_c)\| \ll 1$ [25]

$$\tilde{\hat{\mathcal{R}}} \approx \tilde{\hat{\mathcal{R}}}_n \approx \langle \hat{w}^\alpha\hat{\Omega}^{-1}\hat{\Phi}(\hat{\Omega})\rangle / \langle \hat{w}^\alpha\hat{\Phi}(\hat{\Omega})\rangle. \qquad (5.1)$$

This formula holds for any initial matrix $\tilde{\hat{W}}_i$ and, in particular, for s-fluctuations, if $\|\hat{\tau}_e\| \sim 1/w_c \ll 1/\|\hat{\Omega}\|$. It can easily be obtained from eq. (4.7) if one takes into account that $\hat{q}^{-1}\hat{Q} = N_0\hat{w}^\alpha$.

b. Large $\|H_s\|/w_c \gtrsim 1$. Somewhat more complicated SCTL-case $\|H_s\|/w_c \simeq 1$ can be analyzed by expanding $\tilde{\hat{\mathcal{G}}}$ in powers of the parameter $\xi = \|V\|/\|H_s\| \ll 1$. In particular, within the general two-level model [eq. (4.16)] with $V_d = 0$ in the second order in ξ the diagonal and non-diagonal elements of $\rho(t)$ are decoupled and the corresponding elements of $\hat{\mathcal{R}}(t)$ are expressed in terms of the universal function

$$\mathcal{P}_k(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} d\epsilon\, \frac{e^{i\epsilon t}}{\epsilon + k\epsilon/\langle\hat{\Phi}(\epsilon)\rangle} : \qquad (5.2)$$

$$\langle\mu|\hat{\mathcal{R}}(t)|\mu\rangle = e^{-i\omega_\mu t}\mathcal{P}_{k_\mu}(t), \quad (\mu = n, +-, -+), \qquad (5.3)$$

where

$$\omega_\mu = \langle\mu|\hat{H}_s|\mu\rangle, \quad k_n = 2\mathrm{Re}(k_{+-}), \qquad (5.4)$$

and

$$k_{+-} = k^*_{-+} = \tfrac{1}{2}\omega_s^{-2}\langle\mathcal{V}_n\hat{q}^{-1}[1 - \tilde{\hat{W}}_Q(2i\omega_s)]\mathcal{V}_n\rangle. \qquad (5.5)$$

2. Anomalous $V(t)$-fluctuations

The simplest model for anomalous fluctuations can be written as [9]

$$\hat{\Phi}(\epsilon) = (\epsilon/\hat{w})^\alpha, \ (0 < \alpha < 1), \qquad (5.6)$$

where $\hat{w}$ is the matrix of characteristic fluctuation (correlation) rates diagonal in $|x\rangle$-basis. For the sake of simplicity, $\hat{w}$ is assumed to be independent of x, i.e. $\hat{w} \equiv w(= w_c)$ so that one can use formula (4.12) for evaluation of $\tilde{\hat{\mathcal{R}}}_n$. The model (5.6) describes anomalously slow decay of the PDF-matrix $\hat{W}(t) \sim 1/t^{1+\alpha}$ (very long memory effects in the system [9]), for which only the case of non-stationary (n) fluctuations is physically sensible.

For small $\|H_s\|/w_c \ll 1$ [see eq. (5.1)] the model (5.6) yields the expression constituting the important result of the work:

$$\tilde{\hat{\mathcal{R}}}_n = \langle\hat{\Omega}^{\alpha-1}(\epsilon)\rangle\langle\hat{\Omega}^\alpha(\epsilon)\rangle^{-1} \text{ with } \hat{\Omega}(\epsilon) = \epsilon + i\hat{\mathcal{H}}. \qquad (5.7)$$

This expression demonstrates the surprising property of relaxation induced by anomalous noise in the SCTL: the evolution operator $\tilde{\hat{\mathcal{R}}}_n(\epsilon)$ [and $\hat{\mathcal{R}}_n(t)$], which determines relaxation kinetics, is independent of the characteristic rate w.

It is also worth noting that for $\alpha = 0$ and $\alpha = 1$ formula (5.7) describes relaxation kinetics corresponding to the static and fluctuation narrowing limits [1] in which

$$\tilde{\hat{\mathcal{R}}}_n = \langle \hat{\Omega}^{-1}(\epsilon) \rangle \text{ and } \tilde{\hat{\mathcal{R}}}_n = 1/\langle \hat{\Omega}(\epsilon) \rangle, \qquad (5.8)$$

respectively. At intermediate values $0 < \alpha < 1$ the kinetics is represented by a non-trivial combination of the static- and narrowing-like expressions whose relative contribution is determined by α, as it is seen from eq. (5.7).

Of certain interest is the limit $\alpha \to 1$ in which formula (5.7) predicts the Bloch-type exponential relaxation:

$$\tilde{\hat{\mathcal{R}}}_n(\epsilon) \approx [\epsilon + i\hat{H}_s + (\alpha - 1)\langle \hat{\Omega} \ln(\hat{\Omega}) \rangle]^{-1}. \qquad (5.9)$$

The relaxation is controlled by the rate matrix $\hat{W}_r = (\alpha - 1)\mathrm{Re}\langle \hat{\Omega} \ln(\hat{\Omega}) \rangle$, and is accompanied by frequency shifts represented by $\hat{h} = i(\alpha - 1)\mathrm{Im}\langle \hat{\Omega} \ln(\hat{\Omega}) \rangle$. The peculiarity of anomalous relaxation, however, shows itself in the independence of matrices $\hat{W}_r$ and $\hat{h}$ (unlike those in the conventional Bloch equation) from the characteristic rate w of $V(t)$-fluctuations.

3. Anomalous dephasing for diagonal noise

In the simple model (4.18) of diagonal noise the spectrum $I(\omega)$ can be obtained in analytical form in relatively general assumptions on $V(t)$-fluctuations.

a. General SRM and SCTL. In the SCTL (i.e. for large rate w) within the general SRM (4.1) relatively simple expression for $I(\omega)$ can be derived without any assumption on the structure of energy levels (for any number of states) [25]:

$$I(\omega) = \frac{\sin\varphi}{\pi} \frac{\psi_-^\alpha \psi_+^{\alpha-1} + \psi_-^{\alpha-1}\psi_+^\alpha}{(\psi_-^\alpha)^2 + (\psi_+^\alpha)^2 + 2\psi_-^\alpha \psi_+^\alpha \cos\varphi}, \qquad (5.10)$$

where

$$\varphi = \pi\alpha \text{ and } \psi_\pm^\beta = \langle |\omega - 2V_d|^\beta \theta[\pm(\omega - 2V_d)] \rangle \qquad (5.11)$$

with $\theta(z)$ being the Heaviside step-function. In general, this formula is too cumbersome for studying the specific features of the spectrum. Much more clearly they can be revealed with the use of the two-state SRM (see below).

b. Arbitrary rate w in two-state SRM. The two-state SRM (4.17) allows for the analytical analysis of the spectrum $I(\omega)$ for any value of w, i.e. outside the region of applicability of the SCTL:

$$I(\omega) = \frac{2\xi}{\pi\omega_0} \frac{\sin\phi_0}{z_+ z_-(\eta + \eta^{-1} + 2\cos\phi_0)}. \qquad (5.12)$$

In this expression

$$z_\pm = \xi(1 \pm \omega/\omega_0), \text{ with } \xi = \omega_0/(2^{1/\alpha} w), \qquad (5.13)$$
$$\eta = \zeta(z_+)/\zeta(z_-) \text{ and } \phi_0 = \phi(z_+) + \phi(z_-), \qquad (5.14)$$

where

$$\zeta(z) = |z|^\alpha / \sqrt{1 + |z|^{2\alpha} + 2|z|^\alpha \cos(\varphi/2)}, \qquad (5.15)$$
$$\phi(z) = \mathrm{sign}(z) \arctan\left[\frac{\sin(\varphi/2)}{|z|^\alpha + \cos(\varphi/2)}\right]. \qquad (5.16)$$

Figures 1 and 2 demonstrate a large variety of dependencies $I(\omega)$ for different values of the parameter $\xi = \omega_0/(2^{1/\alpha} w)$. In general, the spectrum possesses two peaks at $\omega = \pm\omega_0$ which at $\xi \ll 1$ and $\alpha \to 1$ collapse into one central peak (see next paragraph). Since in accordance with the definition (Sec. IVB) the limit $\xi \ll 1$ corresponds to the SCTL, the collapse of lines for $\alpha \to 1$ looks quite natural [1]. Simple analysis of eq. (5.12) and calculation results displayed in Fig. 1 show that in this limit general spectrum (5.12) reduces to the limiting one confined in the region $|\omega|/\omega_0 < 1$ [see eq. (5.17) and its discussion]. With the increase of ξ, however, the delocalization of the spectrum outside this region is predicted (Fig. 2). The delocalization becomes especially pronounced in the limit $\alpha \to 1$, as expected.

c. SCTL within two-state SRM. In the two-state SRM (4.17) formula (5.10) is significantly simplified to give the same result as eq. (5.12) in the limit $\xi \ll 1$:

$$I(\omega) = \frac{\sin\varphi}{2\pi\omega_0} \theta(y) \frac{y + y^{-1} + 2}{y^\alpha + y^{-\alpha} + 2\cos\varphi} \qquad (5.17)$$

where $y = (\omega_0 + \omega)/(\omega_0 - \omega)$ (see also ref. [11]). According to this formula anomalous dephasing (unlike conventional one [1]) leads to broadening of $I(\omega)$ only in the region $|\omega| < \omega_0$ and singular behavior of $I(\omega)$ at $\omega \to \pm\omega_0$: $I(\omega) \sim 1/(\omega \pm \omega_0)^{1-\alpha}$. For $\alpha > \alpha_c \approx 0.59$ [α_c satisfies the relation $\alpha_c = \cos(\pi\alpha_c/2)$] the formula also predicts the occurrence of the central peak (at $\omega = 0$) [11] of Lorenzian shape and width

$$w_L \approx \omega_0 \cos(\varphi/2)/\sqrt{\alpha^2 - \cos^2(\varphi/2)}: \qquad (5.18)$$

$$I(\omega) \approx (2\pi\omega_0)^{-1} \tan(\varphi/2)/[1 + (\omega/w_L)^2], \qquad (5.19)$$

whose intensity increases with the increase of $\alpha - \alpha_c$ (see Fig. 1a). At $\alpha \sim 1$ the parameters of this peak are reproduced by eq. (5.9) in which $\langle \hat{\Omega} \ln(\hat{\Omega}) \rangle = -(\pi/2)\omega_0$. The origination of the peak indicates the transition from the static broadening at $\alpha \ll 1$ to the narrowing one at $\alpha \sim 1$ [see eq. (5.7)].

It is worth noting that, of course, for systems with complex spectra this transition can strongly be smoothed and almost indistinguishable experimentally.

4. Anomalous dephasing for non-diagonal noise

a. Dephasing in SCTL for $\|H\|/w \ll 1$. The two-state SRM (4.17) enables one to analyze the behavior of the spectrum $I(\omega)$ in the complicated case $\xi_s =$

$\omega_s/w, v/w \ll 1$ (within the applicability region for the SCTL). In this case dephasing is determined by eq. (5.7). After some manipulations one arrives at

$$I(\omega) = \frac{1}{2\pi}\mathrm{Re}\Big[\frac{\Omega_{-1}(i\omega) + r_0^2(i\omega)^{\alpha-1}\Omega_{-\alpha}(i\omega)}{1 + r_0^2(i\omega)^{\alpha}\Omega_{-\alpha}(i\omega)}\Big], \quad (5.20)$$

where

$$\Omega_\beta(\epsilon) = \tfrac{1}{2}[(\epsilon+2iE_0)^\beta + (\epsilon-2iE_0)^\beta], \quad (5.21)$$

$$r_0 = 2v/\omega_s, \text{ and } E_0 = (\omega_s/2)\sqrt{1+r_0^2}. \quad (5.22)$$

The spectrum $I(\omega)$ predicted by eq. (5.20) is depicted in Fig. 3 as a function of $z = \omega/E_0$ for two values of α and different values of the parameter r. This figure demonstrates non-trivial specific features of the shape of $I(\omega)$ depending on the values of α and r. First of all, similarly to the case of diagonal noise, (in the limit $\xi_s = \omega_s/w, v/w \ll 1$) the spectrum $I(\omega)$ is localized in the region $|\omega| < E_0$ for all values of α. Outside this region $I(\omega) = 0$.

The behavior of $I(\omega)$ significantly changes with the increase of α:

1) At small $\alpha \lesssim 0.6$ the spectrum consists of three peaks (see Fig. 3a): the central peak at $\omega = \omega_c = 0$ and symmetric edge peaks at $\omega = \omega_\pm = \pm E_0$ (at the spectrum edges), in vicinity of which the behavior of $I(\omega) \sim 1/|\omega - \omega_\mu|^{1-\alpha}$, where $\mu = c, \pm$. The intensity of the central peak decreases as α is increased.

2) For large $\alpha \gtrsim 0.6$ each of two symmetric peaks at $\omega = \pm E_0$ split into two ones, so that the spectrum possesses five peaks: at $\omega = \omega_c = 0$, at $\omega = \pm E_0$ and at $\omega = \pm\omega_a$ with $\omega_a < E_0$ (see Fig. 3b). Moreover, the intensity of three original edge and central peaks (at $\omega = \pm E_0$ and $\omega = 0$) decreases as $\alpha \to 1$ while the intensity two additional peaks increases. Besides, the two peaks at $\omega = \pm\omega_a$ approach each other, i.e. $\omega_a \to 0$ with the increase of r (as it is shown in Fig. 3b), and in the limit $r \gg 1$ collapse into one peak.

b. Dephasing in SCTL for large $\omega_s/w \gtrsim 1$. The model (4.19) reveals some additional specific features of the kinetics of phase relaxation in the case of not very large w, when $\xi_s = \omega_s/w \gtrsim 1$. For example, as it is seen from eqs. (5.2) and (5.3), in the limit $\|H_s\| \sim \omega_s \gtrsim w$ matrix elements $\langle\mu|\mathcal{R}(t)|\mu\rangle$, ($\mu = +-, -+$), which describe phase relaxation are given by

$$\langle\mu|\mathcal{R}(t)|\mu\rangle = e^{-i\omega_\mu t}E_\alpha[-k_\mu(wt)^\alpha], \quad (5.23)$$

where

$$E_\alpha(-z) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} dy\, \frac{e^y}{y + zy^{1-\alpha}} \quad (5.24)$$

is the Mittag-Leffler function [26]. In this case the spectrum

$$I(\omega) = I_0(\omega_+) + I_0(\omega_-), \text{ where } \omega_\pm = \omega_s \pm \omega \quad (5.25)$$

and

$$I_0(\omega) = \frac{\sin\varphi}{\pi}\frac{\sin\phi_n}{|x|(|x|^\alpha + |x|^{-\alpha} + 2\cos\phi_n)} \quad (5.26)$$

with $\varphi = \pi\alpha$,

$$x = \omega/(|k_{+-}|^{1/\alpha}w), \quad n_0 = (\pi|k_{+-}|^{1/\alpha}w)^{-1}, \quad (5.27)$$

and

$$\phi_n = \frac{\varphi}{2} + \mathrm{sign}(x)\arctan\Big[\frac{2^{\alpha^{-1}}\sin(\frac{1}{2}\varphi)}{2^{\alpha^{-1}}\cos(\frac{1}{2}\varphi) + \omega_s/w}\Big]. \quad (5.28)$$

Formulas (5.25)-(5.28) predict singular behavior of $I(\omega)$ at $\omega \sim \pm\omega_s$: $I(\omega) \sim 1/|\omega \pm \omega_s|^{1-\alpha}$, and slow decrease of $I(\omega)$ with the increase of $|\omega \pm \omega_s|/\kappa \gg 1$: $I(\omega) \sim 1/|\omega \pm \omega_s|^{1+\alpha}$.

In the limit $\xi_s = \omega_s/w \ll 1$ $\phi(x) \approx \pi\alpha\theta(x)$ so that $I_0(\omega) \sim \theta(\omega)$. This means that for $\xi_s \ll 1$ the spectrum $I(\omega)$ is localized in the region $|\omega| < \omega_s$ and looks similar to $I(\omega)$ for diagonal dephasing at $\alpha < \alpha_c$ and $\xi \ll 1$ (see Fig. 1a). For $\xi_s \gtrsim 1$, however, $I(\omega)$ is non-zero outside this region as well, moreover, in the limit $\xi_s \gg 1$ the spectrum $I_0(\omega)$ becomes symmetric: $I_0(\omega) = I_0(-\omega)$. Such dependence of $I(\omega)$ on ξ_s is also very similar to $I(\omega)$-dependence on ξ found above in the case of diagonal noise.

It is interesting to note that for $\xi_s \ll 1$ functions $\langle\mu|\mathcal{R}(t)|\mu\rangle$ and $I(\omega)$ are independent of w [in agreement with eq. (5.7)] since $k_\mu \sim (\omega_s/w)^\alpha$ and $k_\mu(wt)^\alpha \sim (\omega_s t)^\alpha$. In the opposite limit, however, $k_\mu \sim w^0$ so that the characteristic relaxation time $\sim w^{-1}$.

5. *Anomalous population relaxation*

Specific features of anomalous population relaxation can be analyzed with the model of non-diagonal noise (4.19).

In particular, in the limits $\|H_s\| \sim \omega_s \gtrsim w$ and $1-\alpha \ll 1$ with the use of eqs. (5.2),(5.3) and (5.9) one gets

$$N(t) = E_\alpha[-k_n(wt)^\alpha] \text{ and } N(t) = e^{-w_\alpha t}, \quad (5.29)$$

respectively, where $E_\alpha(-x)$ is the Mittag-Leffer function defined above and $w_\alpha = k_n(\alpha \to 1)w \sim 1-\alpha$. The first of these formulas predicts very slow population relaxation at $t > \tau_r = w^{-1}(k_n/w)^{1/\alpha}$: $N(t) \sim 1/t^\alpha$. Similar to $I(\omega)$ the function $N(t)$ is, in fact, independent of w for $\xi_s = \omega_s/w \ll 1$ because in this limit $k_n \sim (\omega_s/w)^\alpha$. In the opposite limit $\xi_s > 1$ the characteristic time population relaxation is $\sim w^{-1}$ since k_n is independent of w as in the case of phase relaxation.

For $\|H_s\|, \|V\| \ll w$ one obtains [25]

$$N(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} d\epsilon\, e^{\epsilon t}\,\frac{\epsilon^{\alpha-1} + r_0^2\Omega_{\alpha-1}(\epsilon)}{\epsilon^\alpha + r_0^2\Omega_\alpha(\epsilon)}, \quad (5.30)$$

where $\Omega_\beta(\epsilon)$ and r_0 are defined in eqs. (5.21) and (5.22), respectively.

It is easily seen that in the corresponding limits the expression (5.30) reproduces formulas (5.29) with $k_n \approx 2^{\alpha-1}\cos(\pi\alpha/2)(E_0/w)^{\alpha}$ and $w_\alpha \approx \pi(1-\alpha)v^2/E_0$. Outside these limits $N(t)$ can be evaluated numerically (some results are shown in Fig. 4). In general, $N(t)$ is the oscillating function (of frequency $\sim E_0$) with slowly decreasing average value and oscillation amplitude: for $\tau = E_0 t \gg 1$ $N(\tau) \sim 1/\tau^{\alpha}$ (except the limit $\alpha \to 1$). At large $\tau = E_0 t$ one can estimate the asymptotic behavior of $N(t)$:

$$N(\tau) \approx \frac{2}{\pi}\Gamma(\alpha)\Big[2^{\alpha}\sin(\tfrac{1}{2}\varphi)r_0^{-2} + \sin\varphi\frac{2^{-\alpha}r_0^2}{2+2^{\alpha}r_0^2}\cos(2\tau+\tfrac{1}{2}\varphi)\Big]\frac{1}{\tau^{\alpha}}. \quad (5.31)$$

6. Fractional Bloch equation

The kinetic dependencies found in this section for $\|V\|/\|H_s\| \ll 1$ and expressed in terms of the Mittag-Leffler function are conveniently represented in the form of the equation similar to the conventional Bloch equation for the density matrix but with the fractional derivatives. It is easily seen that the kinetic functions (5.23) and (5.29) can be considered as solution of the equation

$$d\hat{\mathcal{R}}/dt = -i\hat{H}_s\hat{\mathcal{R}} - w^{\alpha}\hat{k}[{}_0\hat{D}_t^{1-\alpha}]_s^{\times}\hat{\mathcal{R}}, \quad (5.32)$$

where

$$[{}_0\hat{D}_t^{1-\alpha}]_s^{\times}f = \frac{1}{\Gamma(\alpha)}e^{-i\hat{H}_s t}\frac{\partial}{\partial t}\int_0^t d\tau\frac{e^{i\hat{H}_s\tau}}{(t-\tau)^{1-\alpha}}f(\tau) \quad (5.33)$$

is the modified Liouville-Riemann fractional integral operator, and

$$\hat{k} = \textstyle\sum_{\mu}|\mu\rangle k_{\mu}\langle\mu|, \quad (\mu = +-, -+, n). \quad (5.34)$$

This equation generalizes the well known classical expressions [9] to the quantum processes.

7. Weakly anomalous fluctuations

The analysis presented above shows that the effect of the anomalous noise, i.e. fluctuating interaction [whose correlation functions is anomalously long tailed: $P(t) \sim t^{-\alpha}$ with $0 < \alpha < 1$], on quantum systems can be very strong, manifesting itself in anomalous relaxation kinetics. With the increase of α up to $\alpha > 1$ the effects of anomaly of interaction fluctuations become weaker but, nevertheless, they still manifest themselves in the relaxation kinetics.

To clarify these effects we will briefly discuss the model in which

$$\Phi(\epsilon) = (\epsilon/w) + \zeta(\epsilon/w)^{1+\alpha}, \quad (5.35)$$

where $0 < \alpha < 1$, and w and ζ are the constants with $\zeta \ll 1$ [small value of ζ ensures that $W(t) > 0$]. This $\Phi(\epsilon)$ corresponds to the waiting time PDF-matrix $\hat{W}(t)$ for which the average time $\hat{\tau}_e = \langle t\rangle = \int_0^{\infty}dt\, t\hat{W}(t) = w^{-1}$ is finite but the higher moments $\langle t^n\rangle$ with $n \geq 2$ do not exist.

Possible effects of this weakly anomalous noise can be analyzed within the SCTL with the use of eqs. (5.1)-(5.3). For example, in the limit $\|H\|/w \ll 1$ one obtains formula

$$\widetilde{\mathcal{R}} \approx [\epsilon + i\hat{H}_s + \zeta w^{-\alpha}\langle(i\hat{\mathcal{H}})^{1+\alpha} - (i\hat{H}_s)^{1+\alpha}\rangle]^{-1}. \quad (5.36)$$

which predicts the Bloch-type relaxation of both phase and population, but with the rate

$$\hat{W}_r = \zeta w^{-\alpha}\mathrm{Re}\langle(i\hat{\mathcal{H}})^{1+\alpha} - (i\hat{H}_s)^{1+\alpha}\rangle \quad (5.37)$$

depending on the w as $w^{-\alpha}$, i.e. slower than in the conventional Bloch equation ($\hat{W}_r \sim 1/w$ [1]).

More detailed analysis also demonstrates that in this expression for $\widetilde{\mathcal{R}}$ the terms $\sim w(\epsilon/w)^{1+\alpha}$ are also expected. They lead to the inverse power-type asymptotic behavior of $\langle\mu|\hat{R}(t)|\mu\rangle \sim 1/t^{2+\alpha}$ which, however, is observed only at very long times $t \gg w^{-1}$. This conclusion can easily be clarified with the use of the general formula (5.2) valid in the case $\|H_s\|/w \lesssim 1$, $\|V\|/\|H_s\| \ll 1$ for any model of $\Phi(\epsilon)$. According to this formula for the model (5.35) the kinetics of both phase and population relaxation is similar in its mathematical form to the probability of fluctuations $P(t)$ [see eq. (3.6)] which is, evidently, of power-type behavior at long times: $P(t) \sim 1/t^{2+\alpha}$, in agreement with the above statement.

Formula (5.2) allows for making the following general conclusion on the relaxation kinetics: the kinetics is of anomalous long tailed inverse-power-type behavior for any CTRWA-based model of fluctuations assuming singular $\Phi(\epsilon)$ with brunching points.

B. Anomalous magnetic field effects on RP recombination

In accordance with eq. (4.27), the observables investigated in MARY and RYDMR experiments are expressed in terms of the operator $\widetilde{\mathcal{G}}(r, r_i|\epsilon)$. Within the CTRWA equation for this operator is determined by the model of migration of the mobile radical.

1. Anomalous diffusion and anomalous SLE.

Here we will consider the anomalous diffusion model of migration in which the memory is anomalously long and is described by the operator $\hat{\Phi}(\epsilon)$ (5.6). Notice that in the considered process of spatial diffusion the (diagonal) matrix of characteristic rates $\hat{w}$ in the operator $\hat{\Phi}(\epsilon)$ is actually represented as a distance dependent function:

$\hat{w} = \sum_r |r\rangle w_r \langle r|$. For simplicity, in our further discussion of radical diffusion we assume the rate w_r and the exponent α_r to be independent of r: $w_r \equiv w$ and $\alpha_r \equiv \alpha$. In this case the CTRWA, with $\hat{\Phi}(\epsilon)$ given by (5.6), is known to predict anomalous diffusion [9].

The considered anomalous diffusion of the mobile radical of the RP, evidently, results in non-stationary fluctuations of reactivity $\hat{K}_r$. The effect of these fluctuation is described by the operator $\widetilde{\mathcal{G}}(r, r_i|\epsilon)$ satisfying the non-Markovian SLE (3.34) which can be represented in terms of the so called fractional diffusion equation (for the Laplace transform) as follows

$$\hat{\Omega}_r \hat{\widetilde{\mathcal{G}}} = -\hat{\mathcal{L}}_D(\hat{\widetilde{M}}_r \widetilde{\mathcal{G}}) + \delta(r - r_i), \qquad (5.38)$$

where $\hat{\Omega}_r = \epsilon + \hat{K}_r + i\hat{H}$ and

$$\hat{\widetilde{M}}_r = \hat{\Omega}_r \Phi(\hat{\Omega}_r) = w(\hat{\Omega}_r/w)^{1-\alpha}. \qquad (5.39)$$

In general, solution of the non-Markovian SLE (5.38) with the Smoluchowski-type $\hat{\mathcal{L}}_D$ [see eq. (4.13)] is a fairly complicated (though, in principle, analytically tractable [27]) problem. The most interesting specific features of magnetic field effects, however, can quite clearly be illustrated in some limiting cases allowing for considerable simplification of the obtained general expressions. In our analysis we will concentrate on one of such cases, corresponding to the limit of the deep well u_r and fast diffusion within the this well, which is described by the cage model [27].

2. *The anomalous-cage model.*

Similar to the case of conventional diffusion, fast anomalous diffusion in a large enough and deep potential well $u_r = -u_0\theta(R-r)$, for which $R \gg d$ and $u_0 \gg 1$ leads to rapid relaxation of the initial non-equilibrium spatial distribution of the radical within the well during the time $\tau_D = (R/\lambda)^{2/\alpha}/w$ and formation of the nearly homogeneous quasiequilibrium state (cage) within the well. At longer times $t > \tau_D$ reaction and dissociation are shown to result in the quasistationary decay of this state which is, naturally, independent of the distance r_i of RP creation. At these times, also as for reactions assisted by conventional diffusion, the (anomalous) kinetics of the process under study is described by lowest pole in the expression (3.34) (determined by the lowest eigenvalue of the operator $\hat{\mathcal{L}}_D$) [27]. In what follows this approximation will be called the anomalous-cage model.

Keeping this lowest pole after some algebraic manipulations similar to those presented in ref. [27] one arrives at formula

$$Y_r = \mathrm{Tr}\left[\mathcal{P}_s \hat{l}_r \frac{1}{\hat{l}_r + l_d + (i\hat{H}_z/w)^\alpha} \mathcal{P}_s\right], \qquad (5.40)$$

where [18]

$$\hat{l}_r = \frac{\lambda^2}{R^2} \frac{(\Delta d/\lambda^2)(k_0\hat{\kappa}_S/w)^\alpha}{1 + (\Delta d/\lambda^2)(k_0\hat{\kappa}_S/w)^\alpha}, \;\; l_d = \frac{\lambda^2}{R^2} e^{-u_0}, \quad (5.41)$$

and $\mathcal{P}_s = |S\rangle\langle S|$ is the operator of projection on the singlet ($|S\rangle$) state of the RP.

Formula (5.40) is quite suitable for the analysis of the problem under study. Unfortunately, in general, in the cage model (5.40) the expressions for Y_r are still fairly cumbersome and can be used mainly for numerical estimations.

3. *Specific features of MARY and RYDMR*

To reveal characteristic properties of Y_r-dependence on the parameters of the model we consider simple limiting cases which will be somewhat different for MARY and RYDMR.

a. Analysis of MARY In the considered limit of strong magnetic field B, in which $g_\mu \beta B \gg A_j^\mu$, the effect of spin evolution on reaction yield called MARY can be studied within the ST_0-approximation. In this approximation, which takes into account that in the strong magnetic field limit the contribution of $|T_\pm\rangle$-terms to the reaction yield is negligibly small, the RP spin Hamiltonian is written as

$$H_z^0 = \tfrac{1}{2}\delta\omega(|S\rangle\langle T_0| + |T_0\rangle\langle S|) \text{ with } \delta\omega = \omega_a - \omega_b. \quad (5.42)$$

Detailed analysis demonstrates that, in general, the anomalous-cage model predicts the MARY-dependence on parameters of the spin Hamiltonian similar to that known in the conventional cage model (conventional diffusion assisted processes within the well) [27], however, with replacement of analytical functions by non-analytical ones.

Most important features of non-analytical MARY-dependence on the parameters of the spin Hamiltonian, predicted by the anomalous-cage model, can be demonstrated in the simple limit of relatively weak magnetic interactions: $(\delta\omega/w)^\alpha \ll l_d, \|\hat{l}_r\|$. In this limit one can evaluate MARY with the lowest order of expansion of Y_r [eq. (5.40)] in powers of $\hat{H}_z^0$:

$$Y_r \approx (l_s/l_0) - (l_s/l_0^2)\mathrm{Tr}[\mathcal{P}_S(i\hat{H}_z^0/w)^\alpha \mathcal{P}_S], \qquad (5.43)$$

where $l_s = \mathrm{Tr}(\mathcal{P}_s \hat{l}_r \mathcal{P}_s)$ is the reactivity in the singlet state and $l_0 = l_s + l_d$. Straightforward evaluation with the use of eq. (5.43) gives the expression

$$Y_r = (l_s/l_0) - \tfrac{1}{4}(l_s/l_0^2)\cos(\pi\alpha/2)|\delta\omega|^{\alpha/2}. \qquad (5.44)$$

The non-analytical dependence $Y_r \sim |\delta\omega|^{\alpha/2}$ is just the manifestation of anomalous nature of diffusion within the well (anomalous nature of the cage). Noteworthy is that in the case $\alpha \to 1$ the $\delta\omega$-dependent part vanishes. This is because in eq. (5.43) the spin dependent contribution

to Y_r is taken into account in the lowest order in H_z^0 [$\sim (H_z^0)^\alpha$)]. At $\alpha = 1$, however, the term of this order, linear in H_z, does not contribute to Y_r. The non-zero contribution, evidently, results only from the second order term.

b. Analysis of RYDMR Consideration of the most important specific features of RYDMR can significantly be simplified in the limit of large ST_0-coupling $\omega_{ST_0} = \delta\omega \sim \langle A^\mu \rangle$ [see eq. (4.23)] and relatively weak microwave field ω_1: $(\omega_{ST_0}/w)^\alpha \gg \|l_r\|, l_d$ and $(\omega_1/w)^\alpha \lesssim \|l_r\|, l_d$. In this limit quantum coherence effects on evolution of all states with large splitting ($\sim \omega_{ST_0}$) is negligible [27], i.e. their evolution can be treated with balance equations (equations for state populations).

Coherence effects prove to be important only for four nearly degenerate pairs of states, of type of the TLS discussed above, which describe resonances non-overlapping in the considered limit. These four pairs can be combined into two groups of pairs of these TLSs: $(|\pm\rangle_b|\mp\rangle_a, |T_\pm\rangle)$ and $(|\pm\rangle_a|\mp\rangle_b, |T_\pm\rangle)$, denoted hereafter as $a_\pm$ and $b_\pm$, respectively. Transitions in TLS-pairs $\mu_\pm$, $(\mu = a, b)$, are associated with those in corresponding separate radical μ.

TLS-states $|\pm\rangle_a|\mp\rangle_b$, corresponding to the zeroth z-projection of the total spin ($S_z = 0$), are the same for systems $\mu = a$ and $\mu = b$. However, these systems can be considered as uncoupled because in the studied limit of large ω_{ST_0} significantly efficient transitions in systems a and b occur at different values of ω (i.e. corresponding resonances do not overlap, as it was mentioned above). For this reason it is possible to distinguish the same states $(|\pm\rangle_a|\mp\rangle_b$, belonging to a- and b-systems, and denote them as $|a\rangle$ or $|b\rangle$, respectively (the subscript $\pm$ or $\mp$ can be omitted as it will be explained below).

The assumed initial population of the singlet state reduces to that of the above-mentioned states $|a\rangle$ and $|a\rangle$ (in which $S_z = 0$) with the probability 1/2. Notice that these states are reactive. The reactivity matrices $\hat{l}_r^\mu$ are similar for all systems and quite accurately determined as the two level variant of formula (5.41). These matrices describe reaction with the same rate approximately equal to $l_s/2$, where $l_s = \mathrm{Tr}(\mathcal{P}_s \hat{l}_r \mathcal{P}_s)$ is the reactivity in $|S\rangle$-state.

All the TLSs give the same contribution to the total yield Y_r, differing only in the resonance frequency (ω_a or ω_b) if they correspond to different radicals. Therefore we can combine the identical contributions of the TLSs μ_+ and μ_- into one Y_μ of two times larger magnitude and omit subscripts $+$ and $-$ in the notation of the TLSs and their parameters, as it has been mentioned above. In so doing we arrive at the representation of Y_r in the form

$$Y_r = Y_a + Y_b \tag{5.45}$$

where Y_μ, $(\mu = a, b)$, are given by

$$Y_\mu = \mathrm{Tr}\left[\mathcal{P}_\mu \hat{l}_r^\mu \frac{1}{\hat{l}_r^\mu + l_d + (i\hat{H}_\mu/w)^\alpha} \mathcal{P}_\mu\right] \tag{5.46}$$

with $\mathcal{P}_\mu = |\mu\rangle\langle\mu|$ and $\hat{l}_r^\mu \approx \frac{1}{2} l_s\{\mathcal{P}_\mu, \dots\}$.

For simplicity, we also assume that the microwave field ω_1 is weak enough so that the effects of the ω_1-induced transitions can be treated perturbatively in the lowest order expansion of Y_r in $\|(\hat{H}_\mu/w)^\alpha / \|\hat{l}_{r,d}\| \ll 1$.

In these assumptions the yield Y_μ can be evaluated with approximate expression

$$Y_\mu \approx \tfrac{1}{2}(l_s/l_\mu) - \tfrac{1}{2}(l_s/l_\mu^2)\mathrm{Tr}[\mathcal{P}_\mu (i\hat{H}_\mu/w)^\alpha \mathcal{P}_\mu] \tag{5.47}$$

in which $l_s = \mathrm{Tr}(\mathcal{P}_s \hat{l}_r \mathcal{P}_s)$ and $l_\mu \approx \frac{1}{2} l_s + l_d$.

Calculation using eq. (5.46) gives for the magnetic field dependent part y_r, which is called RYDMR spectrum,

$$y_r(\omega) = y_a(\omega - \omega_a) + y_b(\omega - \omega_b), \tag{5.48}$$

where y_μ, $(\mu = a, b)$, is written as

$$\begin{aligned} y_\mu(\omega) &= -\tfrac{1}{2}(l_s/l_\mu^2)\mathrm{Tr}[\mathcal{P}_\mu (i\hat{H}_\mu/w)^\alpha \mathcal{P}_\mu] & (5.49)\\ &= -\frac{\cos(\pi\alpha/2)}{2}\left(\frac{l_s}{l_\mu}\right)^2 \frac{(\omega_1/w)^\alpha}{(1 + \omega^2/\omega_1^2)^{1-\alpha/2}}. & (5.50) \end{aligned}$$

It is worth noting some important specific features of the RYDMR spectrum (in the case of anomalous diffusion) predicted by eq. (5.50):

1) Unlike conventional Markovian migration, anomalous diffusion leads to the non-analytical dependence of the spectrum on H_μ (i.e. on the parameters of spin hamiltonian) which can be obtained in the lowest order in H_μ. Naturally, as in the case of MARY, the lowest-order value of RYDMR vanishes in the limit $\alpha \to 1$ because at $\alpha = 1$, corresponding to conventional caging, RYDMR amplitude is determined by the second order term of expansion in H_μ.

2) At large ω (at line wings) the RYDMR resonance contributions $y_\mu(\omega)$, $(\mu = a, b)$, decrease as $y_\mu(\omega) \sim 1/\omega^{2-\alpha}$, i.e. slower than the Lorenzian line ($y(\omega) \sim 1/\omega^2$).

3) The width of resonances in the spectrum is determined by the amplitude of microwave field ω_1. In other words these kind of spectra are always measured in the saturation regime [1].

4) At first sight, the fact that the width is determined by ω_1 is a consequence of long memory effects on the processes governed by anomalous diffusion, i.e the absence of the characteristic time in these processes. Therefore in the presence of such time caused, for example, by the conventional intraradical spin lattice relaxation, the width seems to depend on this time. In reality, however, this is not true which can easily be demonstrated in a simple model assuming this time to result from the spin independent decay of radicals with the rate w_0. In this model the magnetic field dependent yield contributions y_μ, $(\mu = a, b)$ are still given by eq. (5.49) but with $(i\hat{H}_\mu/w)^\alpha$ replaced by $[(w_0 + i\hat{H}_\mu)/w]^\alpha - (w_0/w)^\alpha$:

$$y_\mu(\omega) \sim \frac{1}{\omega_1^2 + \omega^2}\left[\mathrm{Re}\Big(w_0 + i\sqrt{\omega^2 + \omega_1^2}\Big)^\alpha - w_0^\alpha\right]. \tag{5.51}$$

It is easily seen that in the limit $\omega_1 \gg w_0$ this expression reproduces eq. (5.50) while in the opposite limit it predicts $y_\mu(\omega) \sim 1/(\omega_1^2 + \omega^2)^{1-\alpha}$. Therefore the presence of the characteristic relaxation time does not lead to the change of the line width of RYDMR spectra slightly changing only the line shape.

VI. CONCLUDING REMARKS

This work concerns the detailed analysis of the specific features of relaxation kinetics in quantum systems induced by anomalous noise. Two types of quantum systems are considered, as examples: two-level systems and radical pairs in a potential well whose recombination is assisted by anomalous diffusion. The analysis is made with the use of the recently developed convenient and powerful method based on the CTRWA and the non-Markovian SLE. It demonstrated some important peculiarities of the kinetics of the processes under study. First of all, the relaxation kinetics in both type of systems proved to be strongly non-exponential. More subtle peculiarities were found in spectral characteristics of these processes: the line shape, its dependence on the parameters of processes, etc.

In addition, the non-Markovian SLE proved to be very efficient in analyzing not only simple TLSs but also multilevel quantum systems. As an example of such systems, recombining RP was considered.

In this work we mainly restricted ourselves to analytical analysis of the processes, however, as it was point out above, the proposed method also allows for significant simplification of numerical treatment of the processes under study, especially in much more complicated multilevel quantum systems: magnetic clusters, magnetic glasses, etc.

Acknowledgments

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Figure captions.

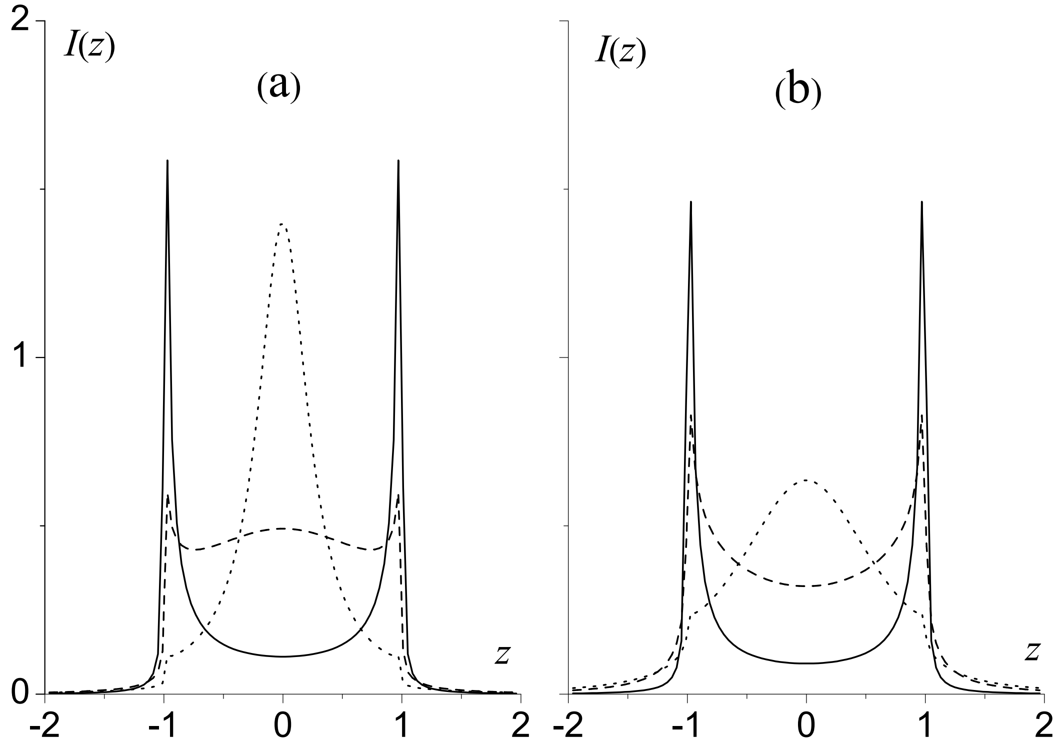
Fig. 1: The spectrum $I(z) = I(\omega)\omega_0$, where $z = \omega/\omega_0$, calculated in the model (4.18) [using eq. (5.12)] for two values of $\xi = \omega_0/(2^{1/\alpha}w)$: $\xi = 0.05$ (a) and $\xi = 0.3$ (b), and different values of α: $\alpha = 0.3$ (full), (2) $\alpha = 0.7$ (dashes), and $\alpha = 0.90$ (dots).

Fig. 2: Same as in Fig. 1 but for $\xi = 0.7$ (a) and $\xi = 1.5$ (b).

Fig. 3: The spectrum $I(z) = I(\omega)\omega_0$, where $z = \omega/E_0$, calculated in the model (4.18) [using eq. (5.12)] for two values of α: $\alpha = 0.5$ (a) and $\alpha = 0.9$ (b), and different values of $r_0 = 2v/\omega_s$: $r_0 = 0.5$ (dots), $r_0 = 1.0$ (dashes), $r_0 = 4.0$ (full) and $r = 8.0$ (dash-dots).

Fig. 4: Population relaxation kinetics $N(\tau)$, where $\tau = E_0 t$, calculated with eq. (5.30) (full lines) for two

values of $r_0 = 2v/\omega_s$: $r_0 = 1$ (a) and $r_0 = 2$ (b), and different values of α: (1) $\alpha = 0.95$, (2) $\alpha = 0.90$, (3) $\alpha = 0.85$, and (4) $\alpha = 0.75$. Straight (dashed) lines represent exponential dependence [eq. (5.29)].


I(z)
(a)
z
I(z)
(b)
z
2
1
0
-2
-1
0
1
2
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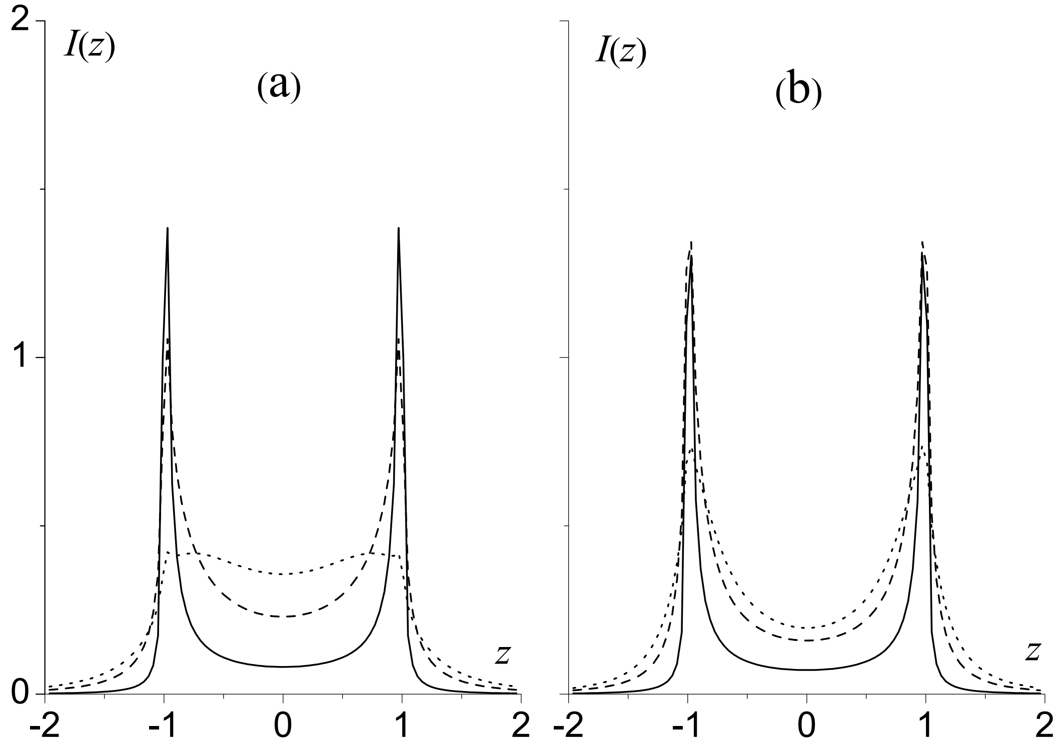
-1
0
1
2



I(z)
(a)
z
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z
0
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1
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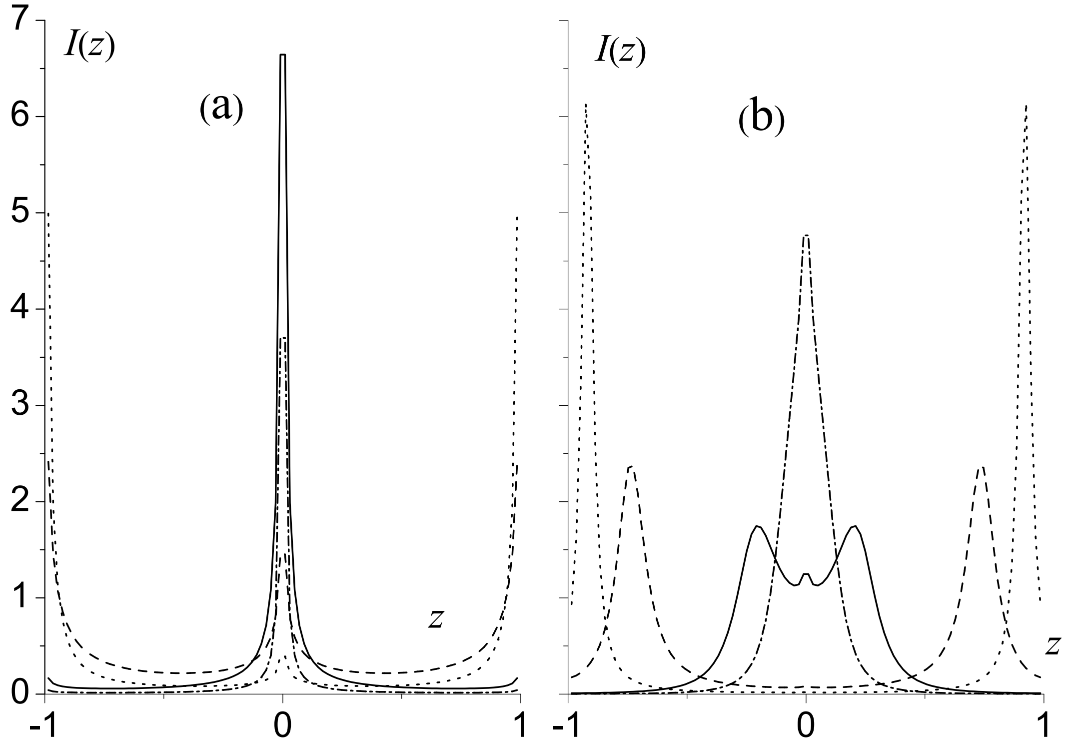

I(z)
(a)
z
I(z)
(b)
z
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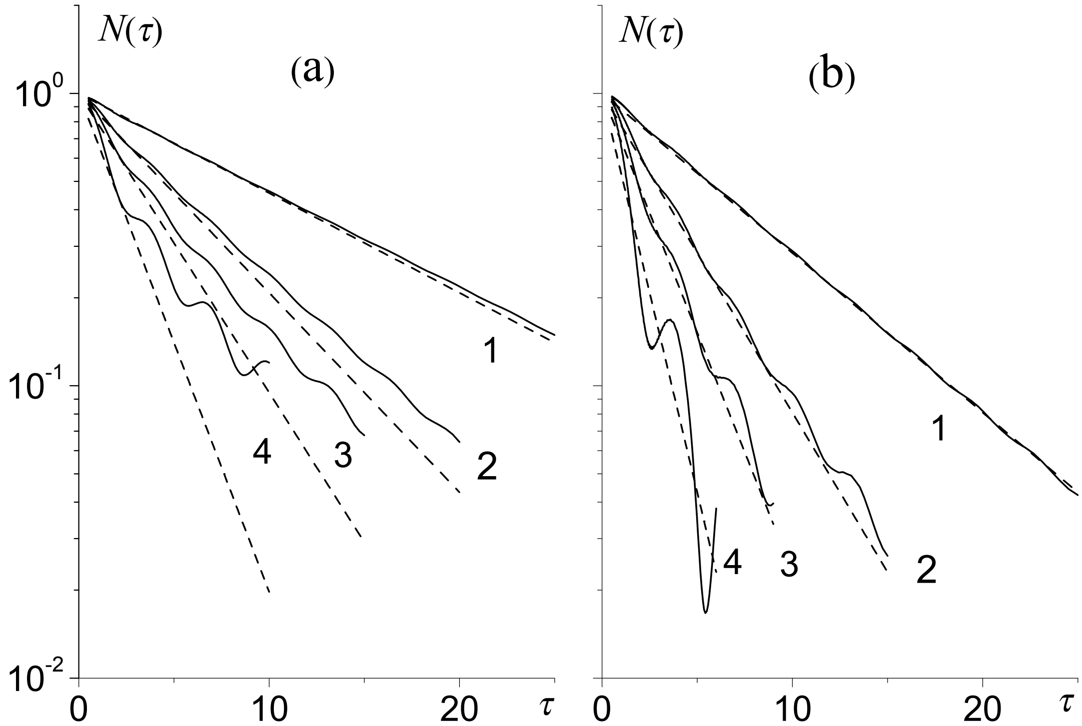
3
4
5
6
7
-1
0
1
-1
0
1



N(τ)
(a)
N(τ)
(b)
10^0
10^-1
10^-2
1
2
3
4
0
10
20
τ